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STABILIZATION OF RESIDUAL CHLORINE

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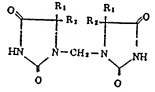
[There are no amendments to this patent.]

Claim

Stabilization of residual chlorine characterized by containing hydantoin compound of the following general formulas (I) or (II) in either hypochlorous acid or an aqueous solution containing a hypochlorite.

(I)



(II)

(In general formula (I) or (II) R_1 and R_2 represent hydrogen, alkyl groups with carbon number 1-4, or ureide groups.)

Detailed explanation of the invention

The present invention concerns the stabilization of residual chlorine. Specifically, the present invention concerns the stabilization of residual chlorine bound to both free residual chlorine and a [illegible]-containing organic compound contained in hypochlorous acid or an aqueous solution containing a hypochlorite.

Chlorine, hypochlorous acid, or hypochlorite has been known as a quick-acting oxidizing agent in low concentrations (10 ppm or less) for controlling microorganisms including bacteria. It

has been used for sterilization or deodorization of water pipes, various types of drainage, cooling water, or for bleaching clothes or pulps. It has been used in low concentrations (residual chlorine concentration: several ppm) for pasteurization or weed control of circulating cooling water contained in a chemical industrial apparatus or a cooling tower, for disinfecting industrial waste water or water discharged from a purifier used in a sewage-treatment plant, or for slime control used in a pulp factory. However, when chlorine, hypochlorous acid, or an aqueous solution containing a hypochlorite are allowed to stand at room temperature, residual chlorine, having oxidation power, releases oxygen, decomposes, then reduces. Because decomposition is accelerated by heat, light, or stirring, residual chlorine in the solution has poor stability. So, when it has been used for the above-mentioned application, the concentration of residual chlorine has been excessively reduced by aging, so that the desired effectiveness has tended to be quickly lost.

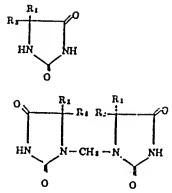
In the case of adding sodium hypochlorite to circulating cooling water used in a chemical apparatus, the cooling water is heated by a heat-exchanger or brought in contact with air in the cooling tower, so that residual chlorine can be suddenly reduced to 1/5-1/10 30 min after the addition. Therefore, amounts of added sodium hypochlorite has to be increased or the frequency of the addition has to be increased, which is economically and mechanically disadvantageous. Corrosion of a cooling-water circulator may be partially accelerated by excessively increasing the amounts of produced chlorine ions. It is a problem that residual chlorine, contained in hypochlorous acid or in an aqueous solution containing a hypochlorite used for

sterilization, weed control, or disinfection, was unstable. Stabilization of residual chlorine is desired to inhibit its reduction and to improve the effects of hypochlorous acid or an aqueous solution containing a hypochlorite as an oxidizing agent.

Regarding stabilization of residual chlorine, it is known that a method employing previous dissolution of isocyanuric acid (30 ppm) in water before using hydrochlorinated isocyanuric acid for disinfecting a pool is effective for inhibiting the reduction of residual chlorine. However, a method using hypochlorous acid or an aqueous solution containing a hypochlorite that was effective in stabilizing residual chlorine has not been developed.

Research on stabilizing residual chlorine contained in hypochlorous acid or an aqueous solution containing a hypochlorite was undertaken by the inventors; it was then found that hydantoin was effective in stabilizing residual chlorine and could complete the present invention. Therefore, it was found that the reduction of residual chlorine due to aging could be greatly inhibited by including hydantoin in the above-mentioned aqueous solution, and that hydantoin could be effective when it was used in amounts of about 0.01 ppm. It was also found that residual chlorine was excessively reduced when [hydantoin] was used in amounts of about 5 ppm or more, and then stabilized and increased. The present invention is based on the above-mentioned knowledge.

Therefore, the present invention involves the stabilization of residual chlorine characterized by containing the hydantoin compound of the following general formulas (I) or (II) in either hypochlorous acid or an aqueous solution containing a hypochlorite.



(I)

(II)

(In general formulas (I) or (II) R_1 and R_2 represent hydrogen, alkyl groups with carbon number 1-4, or ureide groups.)

A method of the present invention is effective in stabilizing free residual chlorine contained in chlorine, hypochlorous acid, an aqueous solution containing a hypochlorite, or residual chlorine bound to a nitrogen-containing organic compound contained in aqueous solution. Examples of hypochlorite include the following, i.e., calcium hypochlorite, magnesium hypochlorite, sodium hypochlorite, and potassium hypochlorite.

Examples of the hydantoin compound of general formula (I) of the present invention include the following, i.e., hydantoin, 5-methyl hydantoin, 5-propyl hydantoin, 5,5-dimethyl hydantoin, 5,5-diethyl hydantoin, 5,5-dipropyl hydantoin, and 5,5-ureide hydantoin. Examples of the hydantoin compound of formula (II) include the following, i.e., 1,1'-methylene bis-hydantoin, and 1,1'-methylene bis-(5,5-dimethyl hydantoin).

In the present invention, one or more types of the above-mentioned hydantoin compound can be contained in either

hypochlorous acid or an aqueous solution containing a hypochlorite by previously dissolving the hydantoin compound in water before adding either hypochlorous acid or an aqueous solution containing a hypochlorite to it, or adding the hydantoin compound to an aqueous solution to which either hypochlorous acid or and aqueous solution containing a hypochlorite has been previously added, or adding the hydantoin [compound] along with either hypochlorous acid or an aqueous solution containing a hypochlorite to water. The minimal amounts of the used hydantoin compound is 0.02 ppm, especially 0.05 ppm or more. The amounts are suitably 0.05-50 ppm. In the case of using it for disinfecting water discharged after waste-water treatment, which does not require residual chlorine for a long time, the concentration of the hydantoin compound is reduced. In the case of residual chlorine desired to be presistent such as in circulating cooling water, the concentration of the hydantoin compound is increased so that the present invention can be effective. The temperature of the aqueous solution is suitably room temperature to 80°C. The pH is suitably 5.5-8.5.

Reduction of residual chlorine contained in an aqueous solution due to aging can be inhibited and the oxidation effect of either hypochlorous acid or a hypochlorite can be improved (sterilization, weed control, or disinfection effect can be extended), by containing small amounts of the hydantoin compound in either hypochlorous acid or an aqueous solution containing a hypochlorite, in the case of the present invention. Therefore, as the frequency of addition or supplement of either hypochlorous acid or a hypochlorite can be reduced, and as the amounts of either hypochlorous acid or a hypochlorite used does not have to be increased, the method is less complicated and economically

advantageous. The method can also reduce corrosion of the apparatus.

In the following, the details of the present invention are explained with application examples. However, the present invention is not specifically restricted by the application examples.

The remaining ratio of residual chlorine described in the specification is given by the following equation:

$$\text{remaining ratio of residual chlorine (\%)} = \frac{\text{concentration of residual chlorine contained in aqueous solution during aging (ppm)}}{\text{concentration of residual chlorine contained in aqueous solution when an oxidizing agent is added (ppm)}} \times 100$$

Application Examples 1-9, Comparative Examples 1-3

A higher bleaching powder containing active chlorine (59.4 wt%) and a sodium hypochlorite aqueous solution containing active chlorine (13.1 wt%) was separately added to water at 25°C, to give each aqueous solution having the residual chlorine a concentration of 3.0 ppm. Then, 5,5-methyl hydantoin (0.02-50 ppm) was added to each aqueous solution, then the pH of each aqueous solution was adjusted to 6.0-8.0 using either citrus acid or sodium citrate. The aging variation of residual chlorine concentration contained in each aqueous solution was measured by the o-toluidine method. Results are shown in Table I. 5,5-methyl hydantoin was not added in the comparative examples.

Table I

		⑤酸化剤	⑥ヒダントイン誘導体濃度 (ppm)	pH	⑦残留塩素濃度 (ppm) 1分間後	2分間後	4分間後	24分間後	48分間後	⑧残留塩素残存率 (%) 1分間後	2分間後	4分間後	24分間後	48分間後
①	実施例 1	次亜塩素酸ソーダ ④	0.02	6.0	2.0	1.8	0.5	0.3	–	–	87	33	17	10	–	–
	〃 2	〃	0.05	〃	2.5	1.8	0.7	0.4	0.1	–	83	36	22	12	3	–
	〃 3	〃	0.1	〃	2.0	2.0	1.0	0.4	0.2	–	67	67	67	28	7	–
	〃 4	〃	1.0	〃	1.3	1.3	0.5	0.2	–	–	26	43	17	7	–	–
	〃 5	〃	10	〃	0.4	0.3	0.3	0.4	0.3	–	13	10	10	13	17	–
	〃 6	〃	50	〃	0.3	0.3	0.3	0.4	0.4	–	10	10	10	13	13	–
②	比較例 1	〃	0	〃	1.3	0.6	0.2	0.1	0	–	40	20	7	3	0	–
①	実施例 7	〃	0.1	6.0	2.3	2.0	1.0	0.6	0.2	–	82	67	33	20	7	–
②	比較例 2	〃 ⑤	0	〃	1.0	0.6	0.3	0.1	0	–	33	20	10	3	0	–
①	実施例 8	次亜塩素酸ナトリウム	10	6.0	0.3	0.4	0.5	0.3	0.3	10	13	17	17	17	17	
	〃 9	〃	25	〃	0.4	0.7	1.1	1.3	1.3	13	23	37	43	43	43	
②	比較例 3	〃	0	〃	1.2	0.7	0.8	0.3	0.1	0	40	23	17	10	3	0

Key: 1 Application example
2 Comparative example
3 Oxidizing agent
4 Higher bleaching powder
5 Sodium hypochlorite
6 5,5 Methyl hydantoin concentration
7 Residual chlorine concentration
8 Residual chlorine remaining ratio
9 After

Application Examples 10-18, Comparative Examples 4 and 5

Each aqueous solution having the residual chlorine concentration of 3.0 ppm was made with an aqueous solution of sodium hypochlorite containing 13.1 wt% active chlorine. Then, hydantoin was added to each aqueous solution to obtain a hydantoin concentration of 0.05-20 ppm, and the pH of each aqueous solution was adjusted to 8.3 or 7.2. The aging variation of residual chlorine concentration contained in each aqueous solution was measured. Results are shown in Table II.

Table II

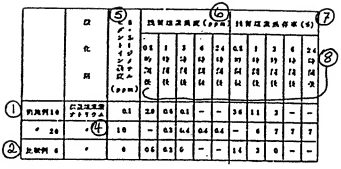
	③ 種類	④ 濃度 M	⑤ ハイダントイン濃度 (ppm)	pH	⑥ 残留塩素濃度 (ppm) 1時間後	2時間後	4時間後	8時間後	24時間後	⑦ 残留塩素濃度保持率 (%) 2時間後	4時間後	8時間後	24時間後	⑧
① 実施例10	5,5-ジメチルヒダントイン	0.05	0.3	8.3	2.8	2.8	2.8	2.7	0.2	97	96	93	93	7
〃 11	〃	0.1	〃	〃	2.3	2.0	1.3	1.0	0.3	83	67	43	33	10
〃 12	〃	0.25	〃	〃	2.8	1.8	1.8	0.5	0.2	97	58	33	17	7
〃 13	〃	1.9	〃	〃	0.3	0.4	0.4	0.5	0.3	10	13	13	17	17
〃 14	〃	20	〃	〃	0.3	0.8	1.3	1.3	1.3	17	27	43	43	43
② 比較例 4	〃	0	〃	〃	2.3	0.8	0.3	0.2	0	40	27	17	8	0
① 実施例15	〃	0.05	17	8.3	2.8	1.3	0.8	0.5	0.1	86	43	27	17	3
〃 16	〃	0.1	〃	〃	2.8	1.5	1.3	1.0	0.3	97	50	43	33	10
〃 17	〃	20	〃	〃	0.3	0.7	0.5	0.5	0.3	10	23	17	17	17
〃 18	〃	20	〃	〃	0.4	0.6	1.0	1.0	1.0	13	20	33	33	33
② 比較例 5	〃	0	〃	〃	2.8	0.7	0.4	0.2	0	93	23	13	7	0

Key: 1 Application Example
2 Comparative Example
3 Oxidizing agent
4 Sodium hypochlorite
5 Hydantoin concentration
6 Residual chlorine concentration
7 Residual chlorine remaining ratio
8 After

Application examples 19 and 20, Comparative Example 6

'A sodium hypochlorite aqueous solution containing active chlorine (13.1 wt%) was added to hot water at 50°C, to given each aqueous solution containing residual chlorine a concentration of 5.5 ppm. Then, 5,5-dimethyl hydantoin was added to obtain a 5,5-dimethyl hydantoin concentration of 0.1-10 ppm, and the pH was adjusted to 7.5 using citric acid. While stirring at a stirring rate of 180 rotations/min and at a water temperature of 50°C, the aging variation of residual chlorine concentration contained in each aqueous solution was measured. Results are shown in Table III.

Table III



Key: 1 Application Example
2 Comparative Example
3 Oxidizing agent
4 Sodium hypochlorite
5 5,5-Dimethyl hydantoin concentration
6 Residual chlorine concentration
7 Residual chlorine remaining ratio
8 After